



Publication number : **0 348 288 B1**

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication of patent specification :
26.08.92 Bulletin 92/35

(51) Int. Cl.⁵ : **C23C 18/12**

(21) Application number : **89401714.4**

(22) Date of filing : **16.06.89**

(54) Method of preparing zirconia film.

(30) Priority : **22.06.88 JP 153875/88**

(43) Date of publication of application :
27.12.89 Bulletin 89/52

(45) Publication of the grant of the patent :
26.08.92 Bulletin 92/35

(84) Designated Contracting States :
DE FR GB

(56) References cited :
EP-A- 0 125 507
US-A- 4 129 434

(73) Proprietor : **NISSHIN STEEL CO., LTD.**
4-1 Marunouchi 3-chome
Chiyoda-ku Tokyo 100 (JP)

(72) Inventor : Izumi, Keiji c/o NISSHIN STEEL Co., Ltd.
Hanshin Kenkyusho No.5, Ishizunishimachi Sakai-shi Osaka 592 (JP)
Inventor : Deguchi, Takenori c/o NISSHIN STEEL Co., Ltd.
Hanshin Kenkyusho No.5, Ishizunishimachi Sakai-shi Osaka 592 (JP)
Inventor : Tanaka, Hidetoshi c/o NISSHIN STEEL Co., Ltd.
Hanshin Kenkyusho No.5, Ishizunishimachi Sakai-shi Osaka 592 (JP)

(74) Representative : Gutmann, Ernest et al
S.C. Ernest Gutmann - Yves Plasseraud 67, boulevard Haussmann
F-75008 Paris (FR)

EP 0 348 288 B1

Note : Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

Description

This invention relates to a method of preparing a zirconia film, and more particularly to a method of preparing a zirconia film by using a zirconium acetylacetonate suspension formed into a sol (or colloidal solution).

Known as methods for preparing zirconia films at low temperatures are (1) a method in which a substrate is coated with a zirconium alkoxide solution comprising zirconium propoxide or zirconium butoxide, followed by hydrolysis and dehydration condensation (Japanese Patent Publication No. 48865/1984, (2) a method in which a substrate is coated with a zirconium octylate solution followed by thermal decomposition (Japanese Unexamined Patent Publication No. 41770/1986), and (3) a method in which a substrate is coated with an organic solvent solution comprising zirconium acetylacetonate or an organic solvent solution comprising zirconium acetylacetonate and a different type of acetylacetonate metallic complex added, followed by heating at temperatures of not less than 200°C to form it into a zirconia film (Japanese Unexamined Patent Publication No. 76881/1988).

However, in the method (1), hydrolysis and dehydration condensation reaction of zirconium alkoxide proceed extremely rapidly and moreover the moisture in the air cause the reaction to proceed, so that it is difficult to form films with a uniform coating and reproducibility. In addition, an attempt to increase the concentration of an alcohol solution of the zirconium alkoxide to obtain a thick film by the first coating may result in formation of the surface into a gel because of the hydrolysis caused by the moisture in the air to produce a white zirconium gel layer on the zirconium film. For this reason the zirconium film can not be made uniform, and the white zirconium gel layer must be removed before the film can be made uniform. In order for the zirconium gel layer not to be produced, the concentration of the zirconium alkoxide may be lowered to retard the rate of hydrolysis in the air, but a lowered concentration makes it necessary to carry out the coating several times to obtain a thick film, thus increasing the coating times.

In the method (2), on the other hand, the hydrolysis rate of the zirconium octylate is lower than that of the zirconium alkoxide, and hence no gel is formed even when coated with its alcohol solution having a higher concentration (not less than about 25 g/l). No problems may therefore arise if the alcohol solution prepared is completely used every time the coating is carried out, but, when the solution is not completely used, the remaining solution must be used in a short time before it can be reused. The zirconium octylate has also a large molecular weight of the organic acid group with respect to zirconium, and therefore the yield of zirconia is as low as about 19%.

In the method (3), the solution can attain a superior workability and give a thicker film at the first coating than other methods. In this method, however, since the acetylacetonate metallic complex is solid, its solubility to organic solvents such as alcohols and aromatic hydrocarbons is not so good that a suspension thereof can only have a concentration of about 0.05 mol/l. For this reason, the film thickness obtained by the first coating is still insufficient, and it has been necessary for obtaining a thick film to use as a solvent a highly viscous solvent such as methyl cellulose or glycol, or increase the coating times.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a method of preparing a zirconia film with a sufficient thickness by the first coating.

Another object of the present invention is to provide a method of preparing a zirconia film by using a coating solution having a superior shelf stability and achievable of a good workability.

According to the present invention, the method comprises coating a substrate with a zirconium acetylacetonate suspension formed into a sol obtained by carrying out hydrolysis of zirconium acetylacetonate by adding water in an amount of from 10 to 12 mols per mol of zirconium acetylacetonate in an organic solvent solution comprising zirconium acetylacetonate, or an organic solvent solution comprising zirconium acetylacetonate and a different type of acetylacetonate metallic complex added. This method can obtain a thick film at the first coating, and the coating solution used in the method can be stably stored for a long period of time.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The zirconium acetylacetonate ($\text{CH}_3\text{COCHCH}_3\text{CO})_4\text{Zr}$ is a coordinate bond compound, and hence can be formed into a sol by carrying out hydrolysis by adding water, thus making its concentration higher than that in a saturated organic solvent solution. This higher concentration makes it possible to apply the compound in a large quantity than that of a saturated organic solvent solution at the first coating, to provide a thick zirconia film after heating.

The theoretical water quantity necessary for completely hydrolyzing the zirconium acetylacetonate is 4 mols per mol of zirconium acetylacetonate, but the water is added in an amount of from 10 to 12 mols. An amount less than 10 mols can not bring about complete dissolution of the zirconium acetylacetonate, resulting in a formation of a suspension, making it impossible to give a thick film at the first coating. An amount more than 12 mols may result in a white and turbid solution in several minutes after hydrolysis to

produce precipitates, making it impossible to carry out coating.

In an instance where a different type of acetylacetonate metallic complex is added in addition to the zirconium acetylacetonate for the purpose of improving the properties of the zirconia film, it is also hydrolyzed by water and formed into a sol, and thus a thick film can also be obtained. It includes, for example, titanium acetylacetonate, aluminum acetylacetonate, potassium acetylacetonate, and diethylthallium acetylacetonate, which can be readily hydrolyzed.

Thermal decomposition after the coating of the zirconium acetylacetonate (and/or the different type of acetylacetonate metallic complex) formed into the sol, may be carried out at 200°C or more in the same manner as conventionally done. To crystallize the zirconia film, the film may be heated at from 500 to 1,200°C.

EXAMPLES

The present invention will be described below in greater detail by giving Examples.

Example 1

In a butanol suspension of 0.51 mol/l (250 g/l) of zirconium acetylacetonate, water was added in an amount of 10 mols per mol of the zirconium acetylacetonate, followed by stirring with a stirrer to make it into a sol.

Next, into the resulting zirconium acetylacetonate suspension formed into a sol and the suspension (control) having been not formed into a sol, stainless steel sheets (SUS304) of 0.4 mm thick each, subjected to ultrasonic degreasing with acetone, followed by pickling and washing with water, were respectively immersed, and drawn up at a constant rate of 0.1 mm/sec which were then put in an electric furnace heated at 400°C for 10 minutes to form zirconia films on the stainless steel sheets.

The resulting zirconia films had a film thickness of 0.25 µm in the instance where the suspension formed into a sol was used, and 0.05 µm in the instance where the control suspension was used. These films achieved a strong adhesion, and were free from generation of cracks and unevenness of film thickness.

The zirconium acetylacetonate suspension formed into a sol was also allowed to stand for a week in the air (relative humidity: 60 % at 25°C) and thereafter again used, but the same results were obtained as those before it was allowed to stand.

Example 2

In an isopropyl alcohol suspension of 0.25 mol/l (120 g/l) of zirconium acetylacetonate, water was

added in an amount of 11 mols per mol of the zirconium acetylacetonate, followed by stirring with a stirrer to make it into a sol.

Next, using this zirconium acetylacetonate suspension formed into a sol and the suspension (control) having been not formed into a sol, zirconia films were formed on SUS304 stainless steel sheets of 0.4 mm thick each in the same procedures as Example 1, to obtain the results that the zirconia films had a film thickness of 0.13 µm in the instance where the suspension formed into a sol was used, and 0.025 µm in the instance where the control suspension was used.

The stainless steel sheets on which these zirconia films were formed were heated at 800°C for 10 hours, and gains in weight by oxidation was measured to find that they were 0.06 mg/cm² in the instance where the film was formed using the suspension formed into a sol, and 0.11 mg/cm² in the instance where the film was formed using the control suspension.

Example 3

While stirring with a stirrer a butanol suspension of 0.25 mol/l of zirconium acetylacetonate, 0.05 mol/l of titanium acetylacetonate and 0.20 mol/l of aluminum acetylacetonate, water was added in an amount of 12 mols per mol of the total of these acetylacetonate metallic complexes to form the suspension into a sol.

Next, SUS304 stainless steel sheets were respectively coated with the resulting suspension formed into a sol and the suspension (control) having been not formed into a sol, following the same procedures as Example 1, followed by heating to thus form an oxide film comprising ZrO₂, TiO₂ and Al₂O₃ uniformly dispersed. The film formed using the suspension formed into a sol had a thickness of 0.22 µm. On the other hand, the film formed using the control suspension had a thickness of 0.04 µm.

Claims

1. A method of preparing a zirconia film, comprising coating a substrate with a zirconium acetylacetonate suspension formed into a sol obtained by carrying out hydrolysis of zirconium acetylacetonate by adding water in an amount of from 10 to 12 mols per mol of zirconium acetylacetonate in an organic solvent solution comprising zirconium acetylacetonate, or an organic solvent solution comprising zirconium acetylacetonate and a different type of acetylacetonate metallic complex added, followed by heating at a temperature not lower than 200°C to form a zirconia film.

Patentansprüche

1. Verfahren zur Herstellung eines Zirkondioxidfilms, umfassend die Beschichtung eines Substrats mit einer Zirkoniumacetylacetonat-Suspension, die als Sol ausgebildet ist, erhalten durch Durchführung einer Hydrolyse von Zirkoniumacetylacetonat durch Zugabe von Wasser in einer Menge von 10 bis 12 Mol pro Mol Zirkoniumacetylacetonat in einer Zirkoniumacetylacetonat umfassenden Lösung in einem organischen Lösungsmittel, oder einer Zirkoniumacetylacetonat und einen zugegebenen Acetylacetonat-Metallkomplex unterschiedlicher Art umfassenden Lösung in einem organischen Lösungsmittel, gefolgt von Erhitzen bei einer Temperatur nicht unter 200°C zur Ausbildung eines Zirkondioxidfilms.

Revendications

1. Une méthode pour préparer une pellicule de zircone, qui comprend le revêtement d'un substrat avec une suspension d'acétylacétonate de zirconium amenée sous forme de sol par la réalisation d'une hydrolyse d'acétylacétonate de zirconium par addition d'eau, à raison de 10 à 12 moles par mole d'acétylacétonate de zirconium, à une solution d'acétylacétonate de zirconium dans un solvant organique, ou à une solution dans un solvant organique comprenant de l'acétylacétonate de zirconium et un type différent de complexe métallique d'acétylacétonate ajouté, puis le chauffage à une température non inférieure à 200°C pour former une pellicule de zircone.